

## **Lipid Layer-based Corrosion Monitoring on Metal Substrates**

**by Scott Kinlein, Anindya Ghoshal, James Ayers, and Daniel Cole**

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# **Army Research Laboratory**

Aberdeen Proving Ground, MD 21005

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## Contents

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<b>List of Figures</b>	<b>iv</b>
<b>1. Introduction</b>	<b>1</b>
<b>2. Lipid Layer Application Technique</b>	<b>2</b>
<b>3. Progressive Salt Spray Exposure Results</b>	<b>3</b>
<b>4. Summary and Future work</b>	<b>5</b>
<b>5. References</b>	<b>7</b>
<b>Distribution List</b>	<b>8</b>

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## List of Figures

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Figure 1. (a) Uncoated Al 6061 plate prior to corrosion and (b) DPPC lipid coated Al 6061 plate prior to corrosion in salt spray chamber.....	3
Figure 2. (a) Uncoated Al 6061 plate after 3 days in salt fog chamber and (b) DPPC lipid coated Al 6061 plate after 3 days in salt spray chamber.....	4
Figure 3. Comparison of uncoated and coated specimens after 14 days in salt fog chamber .....	4
Figure 4. Comparison of uncoated and coated specimens after 42 days in salt fog chamber .....	5
Figure 5. Plexiglass cover on the Al specimens for accelerated corrosion in the salt fog chamber.....	5

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## 1. Introduction

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Corrosion is a deforming process that costs the United States Department of Defense (DOD) approximately \$23 billion annually and accounts for 23% of all DOD maintenance (1). Exhaustive efforts have been made towards the detection and diagnosis of this issue; however, the problem persists. Corrosion is defined as the process in which a solid (e.g., metal) is eaten away and changed by chemical action (2). This occurs as the material's surface is oxidized in an electrochemical reaction, commonly in the presence of oxygen and water, which initially causes small pits to form. The pits are a result of material loss in the form of metal oxides. As these pits grow, they lead to fractures and cracking in the material, which can compromise the structure and integrity of the material, as well as lead to mechanical failure in equipment (3). The current techniques for corrosion monitoring include electrical resistance (ER) testing, radiographic testing, electromagnetic testing, and electrochemical testing; however, the U.S. Army's "Go Green" initiative has opened the door for research into an environmentally friendly, biologically based corrosion monitoring technique. For this reason, novel research is being conducted on the use of lipid layers in corrosion monitoring.

Lipids are a class of macromolecules that serve as the primary constituent of cell membranes and energy storage centers in living organisms. When phosphorylated, or bonded to a phosphate ( $\text{PO}_4^-$ ) group, they become higher energy (4) amphiphilic molecules capable of forming a bilayer (5). In biological systems, this phospholipid bilayer works with protein complexes to regulate material transport, as well as to send and receive information between cells. While natural phospholipids function in living systems, advances in technology over the past few decades have given scientists the ability to study phospholipids in non-biological laboratory settings. Applications of phospholipid layers to engineering are currently being explored in the form of nonconductive coatings (6) and detection of chemical agents (7), and also in their use as a corrosion inhibitor (8).

The goal of this research is to expand on previous knowledge and explore the use of phospholipids in corrosion monitoring applications. As stated previously, when metal is oxidized, material is lost in the form of metal oxides. Phospholipids have been observed to become more conductive in the presence of certain chemicals, possibly disrupting the bilayer (9). If metal oxides are capable of disrupting and causing degradation of a phospholipid layer, it may be possible to detect and diagnose the extent to which the metal has corroded by measuring this degradation. The methods to characterize the degradation are still being explored.

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## 2. Lipid Layer Application Technique

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Spin-coating these synthetic lipids onto the metal substrate is a very simple process. It was originally speculated that a hydrophobic silica monolayer would be necessary before the lipids would adhere to the metal (not shown). They seem, however, to adhere effectively to the aluminum plates after slightly abrading the surface past the glossy finish and cleaning in an ultrasonic de-ionized water bath. For this experiment, the lipids 1, 2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) were purchased from Avanti Polar Lipids in chloroform solution. The lipids were used without further preparation. Sheet stock of aluminum alloy 6061 was obtained from a machine shop and cut into plates of  $5 \times 5 \times 0.15$  cm dimensions. The plates were cleaned with acetone and placed in an ultrasonic de-ionized water bath before experimentation. The lipids were applied by pipetting drop-wise to a plate until covered and then accelerating to rotation in a spin-coating machine at 1000 rpm for 60 s. The plates were left to sit for 15 min to allow residual chloroform to evaporate from the lipids before any further testing was performed. The plates were then weighed and placed into a probe station to be observed at 100x magnification to assess the quality of the applied lipid film. The Keithley 4200 Semiconductor Characterization System should be used in conjunction with the probe station to conduct electrical resistance and conductivity measurements. The plates should then be placed in a salt fog chamber at constant temperature of 95 °F and let to corrode for 3, 6, and 7 days. Once taken out of the corrosive environment, the plates will then be weighed and placed in the probe station for further electrical resistance and conductivity testing. The data from these methods will then be plotted and analyzed to reveal any correlation between lipid loss, electrical resistivity, and corrosion rate.

The following outlines the steps used in preparing the specimens prior to placement into a corrosive environment, such as a salt spray chamber:

1. Obtain phospholipids and mix into chloroform solution, if not done already. This will be necessary for spin-coating, and chloroform is a well-tested solvent for phospholipids. The phospholipid DPPC was used in this experiment.
2. Cut small metal plates ( $5 \times 5 \times 0.15$  cm) from sheet stock. These will be small enough to use in spin-coating machine, yet thick enough to withstand a stay in the corrosive environment. Aluminum alloy 6061 was the chosen metal for this experiment.
3. Clean the plates with acetone and place them into an ultrasonic de-ionized water bath for 5 min before experimentation. This ensures that lipid coating will be applied to an uncontaminated surface.



4. Place a single plate onto the center of a spin-coating machine specimen axis. Apply lipids drop-wise via glass pipette until the plate is covered (~2 ml). Most of the solution will spin off in a spin-coating machine at high rpm, so covering the specimen is common practice in spin-coating, as it ensures all areas are in initially in contact with the solution.
  5. Accelerate the spin coater to 1000 rpm for 50 s. This has shown to be a valid setup for DPPC lipids on aluminum alloy 6061 plates.
  6. Remove the specimen, and let sit for 10 min to allow any residual chloroform to evaporate.
  7. Observe plates at 10x magnification under an optical light microscope to visually verify that lipid film has been applied. Magnification may vary depending on the metal and phospholipid choice. Use an electrical impedance measurement device to obtain electrical resistance data at different points around the plates. A Keithley 4200 Semiconductor Characterization System (SCS) was used in this experiment, as it allows specific points to be saved and returned to.
  8. Place the plates in a salt spray chamber at 95 °F for varying time intervals.
  9. Once removed from the corrosive environment, again use the impedance measurement device to obtain electrical resistance data at the same points, as done previously.
  10. A chosen method of measuring the lipid layer degradation can then be used to assess the volume of material that has been lost specifically from the coating.
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### 3. Progressive Salt Spray Exposure Results

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The initial surface response to the salt spray chamber was monitored progressively using visual inspection prior to quantitative evaluation techniques. Figures 1–3 compare the uncoated to coated metal substrates up to 14 days of exposure.

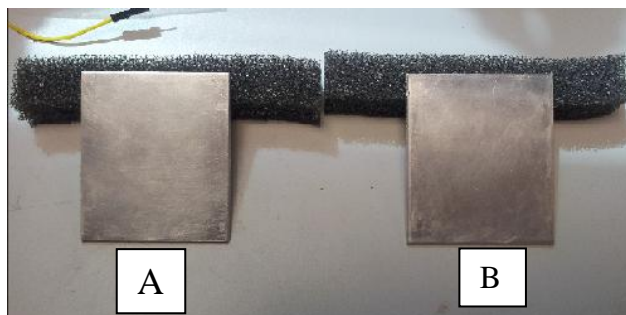


Figure 1. (a) Uncoated Al 6061 plate prior to corrosion and (b) DPPC lipid coated Al 6061 plate prior to corrosion in salt spray chamber.

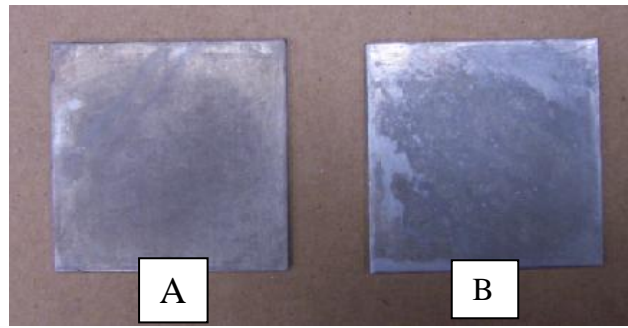


Figure 2. (a) Uncoated Al 6061 plate after 3 days in salt fog chamber and (b) DPPC lipid coated Al 6061 plate after 3 days in salt spray chamber.



Figure 3. Comparison of uncoated and coated specimens after 14 days in salt fog chamber

It is observed that after 14 days, there does not exist on the macroscopic level any visible pitting or corrosion-like presence. Even after 42 days, not much evidence of corrosion has been observed (figure 4). The samples are now placed under plexiglass in the salt fog chamber as shown in figure 5 for accelerated corrosion

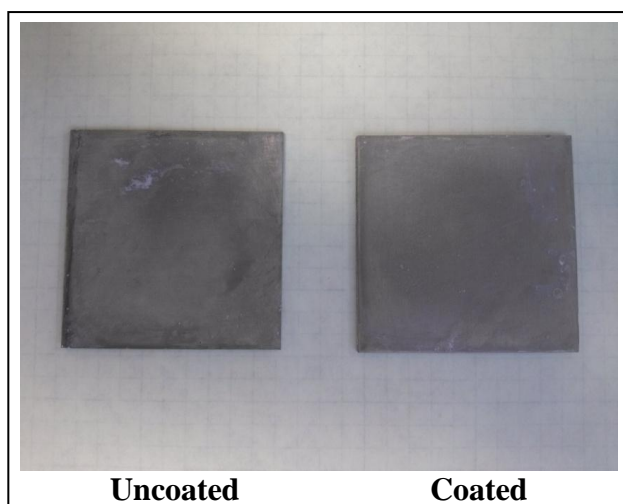


Figure 4. Comparison of uncoated and coated specimens after 42 days in salt fog chamber

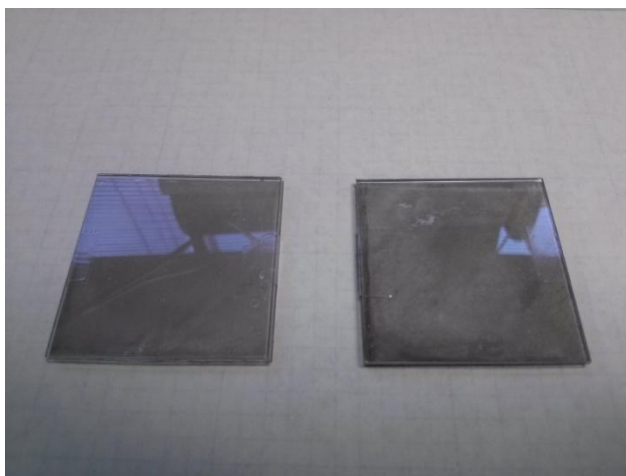


Figure 5. Plexiglass cover on the Al specimens for accelerated corrosion in the salt fog chamber.

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## 4. Summary and Future Work

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A brief description is proposed for corrosion monitoring of metals using phospholipids as a surface coating. Upon corrosion development, quantification techniques such as a Keithley SCS impedance analysis will be used to show that electrical resistivity increases with increasing corrosion. The Keithley 4200 SCS is planned to be used to measure the electrical impedance through the aluminum plates in a four probe setup to get more accurate data. In addition, by creating a grid on the plates and taking readings at different positions, values would be obtained

that are more representative of the sample as a whole. This would be repeated at different time intervals during a stay in the corrosive environment, a plot would be generated showing change in impedance over time. The trend that accompanies the plot should be indicative of corrosion rate.

Prospective methods to characterize lipid layer degradation may include Mass Spectrometry, Atomic Force Microscopy, Surface Profilometry, and Scanning Electron Microscopy. These methods have aspects that would be ideal for determining the surface topography and detecting flaws in the lipid layer on a sub-micron scale. The trend that accompanies lipid degradation data can be used alongside the trend in impedance data and used to estimate corrosion rate.

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